An experimental investigation into quantifying CO_2 leakage in aqueous environments using chemical tracers

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Abstract

Chemical tracers can be an effective means of detecting, attributing and quantifying any leaks to the surface from geological CO_2 stores. CO_2 release experiments have found it difficult to ascertain the fate, or quantify the volume of CO_2 without the application of tracers. However, a significant proportion of global CO_2 storage capacity is located offshore, and the marine environment poses constraints that could limit the success of using tracers. These constraints include uncertainties in the behaviour of tracers in marine sediments and the water column and sampling challenges. However, to date there have been few experimental investigations to address these uncertainties. Here, we used a benchtop experimental setup to explore how effectively methane, a common constituent of captured CO_2 and of reservoir fluids, can aid the quantitation of CO_2 leakage in aqueous environments. The experiment simulated gas leakage into sediments that mimic the seabed, and we measured the partitioning of co-released gases under different environmental conditions and injection rates. We find that the style of seepage and the fate of the CO_2 are affected by the presence of a sand layer and the injection rate. We discuss the implications for leak monitoring approaches, including how tracers may be used to quantify the leak rates and fate of CO_2 in aqueous environments. Our work contributes to ongoing efforts to develop robust offshore monitoring system that will assure operators, regulatory bodies and the public of CO_2 storage integrity.

Keywords: carbon capture and storage, monitoring, offshore, seabed, CO_2 fate

1. Introduction

Most commercial carbon capture and storage (CCS) projects and all pilot scale projects worldwide are located onshore, whilst many future full-chain commercial scale offshore CCS projects are proposed (GCCSI, 2015). It is estimated that 40% of global CO_2 storage capacity is located offshore, and in some regions of the world the majority of storage capacity is located offshore (IEAGHG, 2008). This is particularly the case in Western Europe, where, due to the location of the geological storage resource and the availability of subsurface information, prospective stores are largely located below societally important shelf seas. Legislation and guidelines developed for CCS have set performance requirements to minimize leakage risk (Dixon et al., 2015) and to quantify and remediate any leaks that arise (Dixon et al., 2015; IEAGHG, 2012, 2015). Leakage of CO_2 would impact on a number of stakeholders, incurring financial and environmental costs, and also challenge public acceptance of the technology (Dixon et al., 2015; Feitz et al., 2014). Site selection for geological storage seeks to maximise containment and minimise risk of leakage (Miocic et al.,

2016). However, methods of measurement, monitoring and verification are necessary to demonstrate CO_2 containment, and these approaches must be developed for both onshore and offshore environments. However, in the absence of any industrial analogues, we must look to laboratory and field experiments to develop and test robust monitoring approaches.

Should CO_2 leak from offshore stores and into the marine environment, CO_2 may leak through seabed sediments into the water column. It may dissolve into sediment pore waters and so reach the seabed as either as a dissolved gas, or could remain in its free phase, forming bubbles which rise through the water column. These bubbles might partially or completely dissolve during their ascent through the water column. Otherwise, in the case of shallow waters, poorly mixed water or rapid leak rates, the bubbles might reach the sea surface releasing CO_2 into the atmosphere.

In the terrestrial environment, CO_2 leakage to the surface can occur through dry soils and sediments, water-saturated soils and sediments, or into terrestrial water bodies such as lakes and rivers. CO_2 might be transported as a dissolved constituent of groundwater which could remain dissolved or might be released by ebullition (see Table 1 for definitions of leakage terms). Otherwise, CO_2 might be released as a free phase gas. There is evidence from natural analogues that leakage preferentially occurs in topographic low points (Roberts et al., 2014), and so leakage into or close to streams, ponds, and rivers could be the most likely occurrence in the terrestrial environment (whether these are ephemeral or permanent). Further, the water table depth is observed to affect the characteristics (e.g. distribution and amplitude) of the leakage. In general, low CO_2 fluxes and conditions that favour high CO_2 solubility encourage dissolution and dispersive transport, while relatively high fluxes and conditions that reduce solubility encourages ebullition and bubble transport (Oldenburg and Lewicki, 2006).

Term	Definition
Leakage	Migration in the subsurface away from the primary containment formation, e.g., through a fault or abandoned well.
Seepage	Migration across a boundary such as the ground surface or from subsurface rock or sediments into surface water. Bubble Immiscible volume of a secondary fluid phase (e.g., supercritical, gas, liquid) within a primary connected phase (e.g., aqueous).
Ebullition	Formation of bubbles from a liquid supersaturated with respect to dissolved gases, either in surface water or in groundwater.
Bubble flow, or gas-phase transport	Flow of component(s) as transported in discrete bubbles.
Channel flow	Flow of component(s) as transported in a secondary connected fluid phase within a primary liquid phase.
Dissolution	Uptake of volatile components into solution in the liquid phase.
Advection	Component transport driven by movement of a phase containing the component.
Diffusion	Component transport driven by concentration gradients within a phase.
Dispersion	Component transport by small-scale advective motions and by diffusion that can be modelled collectively as a diffusive process.

Table 1: *Terminology related to gas migration, after (Oldenburg and Lewicki, 2006).*

Detecting and quantifying CO_2 leaks is challenging because CO_2 can be naturally present or generated in the subsurface, biosphere and atmosphere. Chemical tracers that 'fingerprint' CO_2 injected for CCS could allow it to be differentiated from these other natural or background sources (Stalker et al., 2009). The effective application of chemical tracers could provide valuable information about the migration and fate of CO_2 injected for geological

storage. Chemical tracers have already been applied to understand origin, flow and fate of naturally occurring CO_2 systems (Gilfillan et al., 2008; Wilkinson et al., 2009).

Assessment of monitoring options have found tracers to be a low cost and high return technique (Ringrose et al., 2013) and one of the most promising for leak detection and quantification (IEAGHG, 2012). A portfolio of tracers has been proposed for CCS, and several have been developed and tested at CO_2 injection and release experiments and pilot CCS projects worldwide (Jenkins et al., 2015; Mayer et al., 2013; Myers et al., 2013; Serno et al., 2016).

While these approaches have advanced considerably, challenges remain. For example, the majority of onshore CO_2 release experiments conducted around the world to date have found it problematic to estimate the proportion of injected CO_2 that leaked to the surface (Roberts and Stalker, 2017). Furthermore, these have focussed on terrestrial environments; as yet tracers have not been tested for offshore, and there is significant uncertainty about their behaviour in marine environments (Roberts et al, 2017). The capability of tracer monitoring methods to identify, locate, and quantify CO_2 leaks to the seabed must be demonstrated before being applied to commercial scale CCS projects. However, offshore tracer programmes face considerably different challenges compared to onshore projects. For example, the properties of the most suitable tracers might vary due to differences in the fate and impact of CO_2 (and tracers) that leak to seabed, and there will be practical and legal differences around injection and sampling strategy and permitting procedure (Roberts et al, 2017).

Globally, there has been only one sub-seabed CO_2 release experiment conducted to date. The project, known as QICS (Quantifying and Monitoring Potential Ecosystem Impacts of Geological Storage; www.qics.co.uk) aimed to investigate the environmental consequences of a leak and methods for detection. The experiment mimicked small-scale CO_2 leakage into seabed sediments located offshore near to the town of Oban, on the west coast of Scotland. For 37 days CO_2 was continuously released 11 m below the seabed (and ~10 m seawater). CO_2 bubble streams were observed at the seabed only a couple of hours after CO_2 injection started, but it took 34 days for dissolved CO_2 to reach pore waters near the seabed (Taylor et al., 2015). A broad range of approaches were used to monitor the evolution of the seep and its impact on the marine environment, as well as to quantify the fate of released CO_2 (Blackford et al., 2014). Overall, it is estimated that ~15% of the injected CO_2 reached the seabed as a free phase (Blackford et al., 2014) and modelling finds that 14 - 63% dissolved in sediment pore waters (Taylor et al., 2015) but there are considerable uncertainties associated with these numbers (Blackford et al., 2014). This illustrates the need to develop and test techniques to measure and quantify the fate of injected CO_2, and it has been proposed that chemical tracers could quantitate these processes further (Blackford et al., 2015). As the project found significant potential for buffering by carbonate compounds in the seabed sediments, which supressed the changes to chemical parameters (i.e. pH and conductivity) that might be expected to arise from a CO_2 leak (Blackford et al., 2014), we must look to other approaches to identify any leaked or leaking CO_2. Furthermore, chemical changes provided no information about CO_2 attribution and so for future experiments it may be more reliable to apply chemical tracing using stable isotope composition (if CO_2 source is significantly different from background) or inert tracers (Blackford et al., 2015). As such the QICS project highlighted the difficulties attributing and understanding the fate of injected CO_2 without chemical fingerprinting approaches, even with a very high intensity monitoring programme.

To this end, we used a benchtop experimental setup to simulate gas leakage across the sediment-water interface of terrestrial water bodies, and into the atmosphere. We used methane, CH_4, as a tracer. CH_4 is a common constituent of CO_2 from various capture sources

(Porter et al., 2015) and of reservoir fluids (Soltanian et al., 2018) as it is very expensive to separate completely from the CO_2 stream. Furthermore, it is present at trace levels in the atmosphere, and could therefore readily act as a low-cost tracer that could aid identification, attribution and quantitation of leaked CO_2 see e.g. (Klusman, 2018; Roberts et al., 2017). We used an in-line infra-red (NDIR) based cavity ring down spectrometer to continuously measure the gas concentrations in the headspace. From this, we deduced the partitioning of co-released gases in the bubble streams to explore how leak rates can be usefully constrained, and the best approaches of doing so. This work contributes to ongoing efforts to improve effective environmental monitoring techniques for geoenergy systems of the future.

2. Methods

2.1 Equipment

We designed a laboratory experiment that simulated leakage of CO_2-CH_4 mixture into sediments that mimic aqueous environments (i.e. lake or sea bed). The experimental set up is shown in Figure 1. A high-density polyethylene container (approximately 1050 mm diameter at top and 300 mm high) was partly filled with 80 kg of cleaned quartz silica sand (0.1 – 0.2 mm particle size) and ~60 L of distilled water. For the control experiments either the sand or sand/water was removed. In the water only control experiment, 80 L of water was used giving it a similar amount of headspace as the sand/water experiments. A lid constructed from an acrylic sheet isolated the environment within the container from the atmosphere. Three ¼" Swagelok bulkheads in the lid powered a fan (to circulate the air inside the container) and allowed a recirculating loop to a gas analyser. One 1/16" Swagelok bulkhead supplied a gas mixture (78.7(CO_2):21.3(CH_4) by volume) via 2.64 m length of 1/16" tubing. The tube outlet was adhered to the center of the base of the container. The gas flow from a G-size cylinder was controlled by a calibrated Bronkhorst® EL-FLOW mass flow controller (nominally 0 to 10 mL for N_2). We used a Picarro G2201-i CRDS (cavity ring down spectrometer) gas analyser which is capable of ppb resolution readings for CH_4 and CO_2 at concentrations up to 1000 ppm and 4000 ppm respectively (in high range mode). The isotope modes of this instrument were not used for the purposes of this research.

'Seabed' conditions were selected to mimic the QICS environment, with water depth and flow rate ~ 100^{th} of the scale, and sediments similar to the 2m thick fine sand at QICS (Unit B). For this unit, the median and mode particle size are 75 and 100 µm respectively, and 200 um is the maximum (90th percentile) particle size. In our experiment, we use clean silica sand with a particle size ranging from 80 to 130 µm. The density of the sand is 1.62 g/cm^3 and the porosity ~ 40.4%. Initially we used glass beads (specifically, BALLOTINI metal finishing beads) to completely control grain size distribution and mineralogical composition, however preliminary tests with the beads were problematic; they were basic and so adsorbed CO_2.

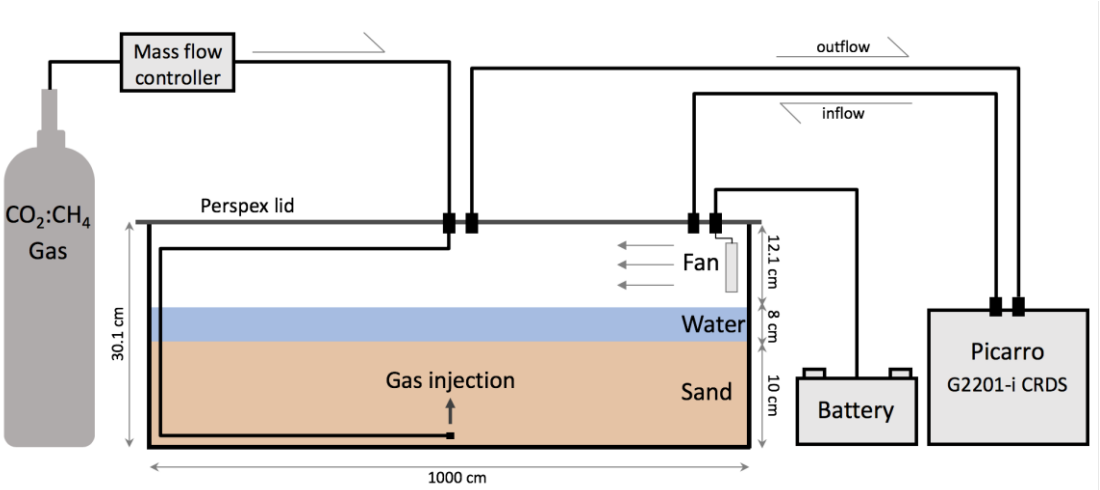


***Figure 1**: Experimental setup of the simulate leakage experiment. The Picarro system continually recirculates the air in the container to monitor the changes in concentration as a known amount of a methane/carbon dioxide mixture are added via the flow meter and the headspace is stirred utilising a small fan. The pond is slightly wider (1053 cm) at the top than at the base (1000 cm). This is accounted for in our volume calculations.*

2.2 Experimental procedure

Before each experiment was conducted, the system was first purged of any residual CH_4 and CO_2 from previous experiments by opening the container to the ambient surroundings and allowing atmospheric equilibrium to establish over several days. The lid was then replaced (effectively sealing the system) and the Picarro recirculated air in the headspace for several hours to confirm that the gases in the system reflected atmospheric levels (i.e. approx. 400 ppm CO_2; 1.78 ppm CH_4). The gas inlet from the CH_4:CO_2 mixture was then temporarily disconnected from the reservoir and gas was flowed through the line for ~15 minutes to purge the 1/16" pipe of 'old' gas (which may have stratified). The fitting was then reconnected, starting the experiment.

Gas was continuously injected at the specified flow rate until the concentration of gas in the headspace exceeded the reliable tolerance threshold of the Picarro CRDS analyser (1500 ppm for both CH_4 and 2000 ppm for CO_2). The duration of the experiment was therefore dependent on gas injection rate. Gas concentration measurements were acquired continuously at a rate of one sample every 1 to 5 seconds. Experiments were performed for three experimental conditions: (A) an empty container (i.e. the control experiment), (B) a container with 80 L water only, and (C) a water/sand system (see Table 2).

For experiments (C) 80 L of water was first added to the reservoir and then 80 kg of sand was poured into the water, allowed to settle over 48 hours, then graded approximately level if needed. These steps ensured complete saturation of the sand with water, minimised sediment disturbance, and avoided the formation of sediment structures or discontinuities during set-up (we determined that the alternative, mixing the sand to ensure saturation, affects the sediment structure more). The 1/16" tubing was adhered to the centre of the container so that gas release always occurred at the same location, and to avoid disturbing the sediment structure (and so creating preferential leak paths) when inserting the tubing. As a control, before the experiment started we checked that there was negligible change in the concentrations of CO_2 or CH_4 when no gas was flowing and the pond lid was closed. This confirmed that the system was stable, and that neither the sand or water (or e.g. any contaminant microbes) produced or consumed either of the gases. During the experiments,

the fan gently recirculated the air in the headspace. We investigated flow rates from 0.88 to 8.8 mL/min and repeated each experiment a minimum of 3 times.

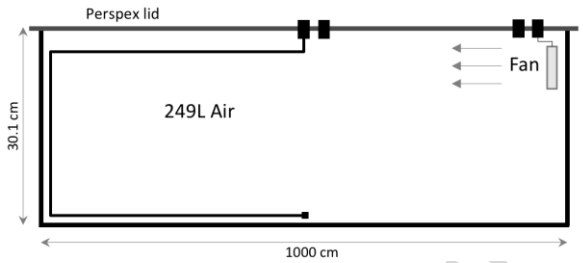
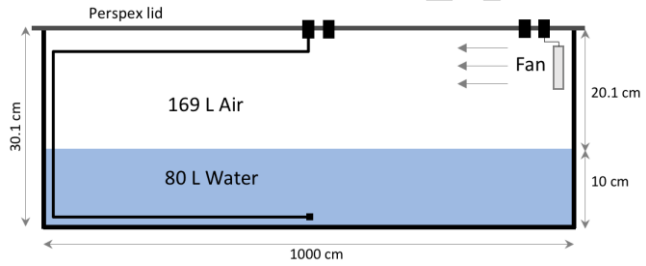
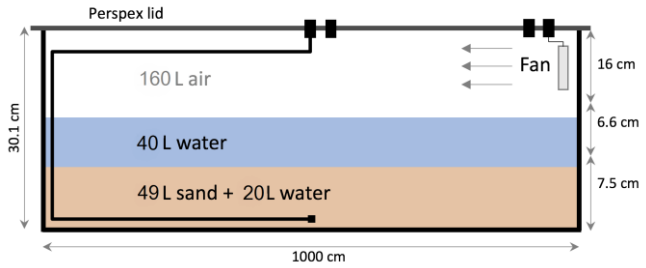
	Experiment	Environment properties	Flow rate(s) mL/min
A	Dry (no water, no sand)		0.88
B	Water only		0.88
C	Water and sand		(1) 0.88 (2) 1.76 (3) 4.40 (4) 8.80

***Table 2**: Summary of experimental environments. Experiment A is a control experiment which assessed whether the system was closed and that the gas concentrations raised as predicted. Flow rates were constant for experiments A & B but were varied for experiment C.*

3. Results

3.1 Observations

As shown in Figure 2, released gases were detected soon after gas injection initiated, with a response time of less than 30 seconds. The presence of sand and/or water in experiments B and C reduced the volume of the tank headspace (by 40% for B, and 68% for C). The reduction in the headspace volume will cause a more rapid increase in the gas concentration; however, the effects of water on the behaviour of the gases needs to be considered as well for experiments B and C.

Gas bubbling through the water column could be observed in experiments B and C via the perspex lid. For experiment B, gas bubbles were released from the pipe end at regular intervals (every ~0.8 s for 0.88 mL/min injection rate). The bubbles were small; their diameter no larger than the 1/16" pipe. For experiments C, gas bubbling from the sand was intermittent and irregular (i.e. periodic). At 0.88 mL/min injection rates, periods of no

bubbling could last several seconds or up to 15 mins and were followed by a period of steady or intermittent bubbling (see Figure 2E). For higher gas injection rates the bubbling remained intermittent but the periods of no bubbling were much shorter. Gas bubbling was almost continuous for experiments C4, 8.8 mL/min injection rate, see Figure 2F. In experiments C, the gas bubbling occurred in the pond centre, directly above the end of the injector pipe. The bubbling had developed a small pit or hollow in the sand by the end of the experiment. That the seep point in our experiments was directly above the injector suggests that there were no structures in the sand that influenced the gas flow.

3.2 Data processing

The irregular and intermittent bubbling in experiments C led to some complexity in the data processing. Each bubble that reached the water surface caused a rapid rise in gas concentration which was otherwise stable (i.e. not increasing) between bubbles. As a result, the change in gas concentrations in the headspace was non-continuous.

The rate (quantified as ppm/hr) of change in the gas concentration of the headspace (as gas flows into the system) was determined by first fitting the concentration vs. time data to a 4th degree polynomial (where $R^2 > 0.999$) and then analytically calculating the 1st order derivative. The result, a smoothed rate profile for gas concentrations, removed the short-term noise in the data and any artefacts caused by the intermittency of bubbles, and so allowed us to understand the change in the rate over the time scale of the experiment. The 1st order derivative of polynomial fits are given in Figur

e 3.

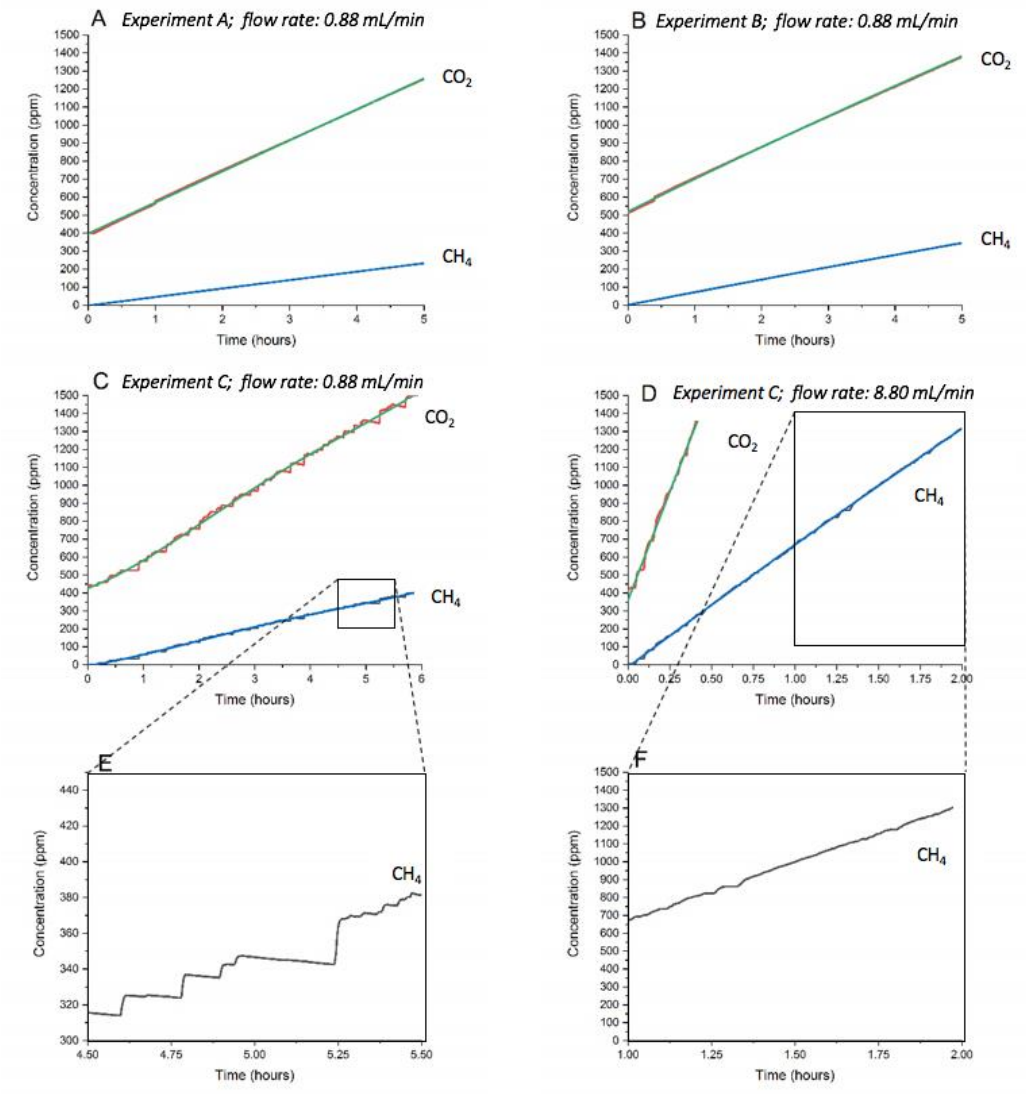


***Figure 2**: Results of CO_2 and CH_4 concentrations for experiment A (A), B (C), C1 (C), and C4 (D). Zoomed results from experiment C1 (E), and C4 (F). Images A, B, C and D include 4th degree polynomial fit, necessary to adjust results for the quantitation problems that arose from the intermittency of bubbling in experiments C1-4 (for A, B and D, the polynomial fit is very close to the original data so it is hard to discern the difference).*

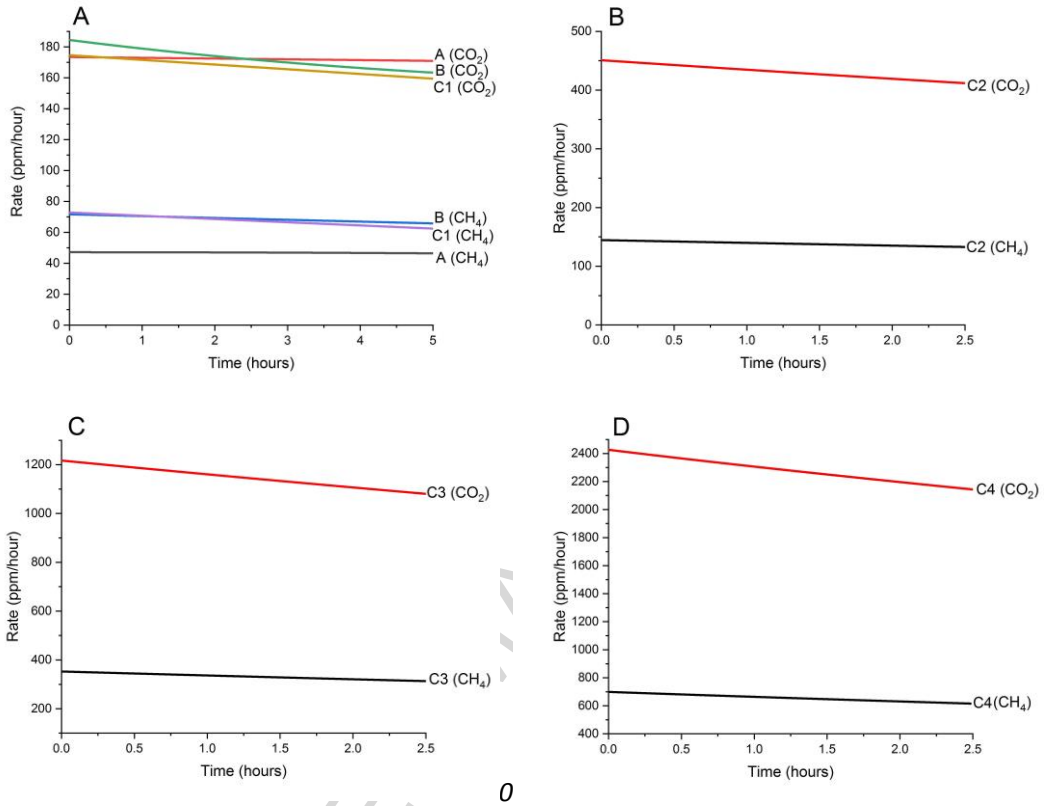


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***Figure 3:** (A) Rate of change of CO_2 and CH_4 concentrations for experiments A-C for 0.88 mL/min injection rate. (B),(C),(D) Rate of change of gas concentrations for 1.76, 4.40 and 8.80 mL/min injection rates in experiment D, E and F, respectively. Note the different Y axis scales for A-D.*

3.3 Leakage from the tank

During the experiment, minor leakage from the tank equal to the injected gas flow rate was expected to maintain pressure equilibrium inside and outside the experimental tank. With good mixing in the tank (from the fan) and a small amount of gas injected relative to the volume of the tank, the effect on concentration, or the rate of change in gas concentration, due to leakage from the tank was expected to be minor.

For control experiment A, the rate of increase in gas concentrations was relatively constant with only a very slight decrease over time. The smaller headspace volume in experiments B and C compared to experiment A caused the rate of leakage from the tank to be marginally more rapid. Still, the effect of leakage from the tank is minor, in part due to the small volumes of injected gas (<1.3 L over the total duration of experiment C4).

3.4 Fate of the injected gas

We calculated the fate of the injected gases by comparing the observed rate of increase in gas concentrations in the headspace (R_{obs}) with the rate predicted (R_{hyp}) if *none* of the gas dissolves into the water or leaks from the tank for the given gas mixture

(78.7(CO_2):21.3(CH_4)) and flow rate (0.88 mL/min). As shown in Table 2, the hypothetical and observed rate of gas increase are very similar. i.e. ~all of the injected gas was immediately detected. The ratio of the initial CO_2:CH_4 rate corresponds to the injected gas mixture (78.7(CO_2):21.3(CH_4) by volume).

We used control experiment A as the baseline for zero dissolution and zero residual trapping (as it contains no sand and no water) and compare the rates observed in experiments B and C to this baseline to find the quantity of gas that does not leak to surface. In experiments B, 26% of the injected CO_2 does not leak to the headspace. For C1, a little less CO_2 leaks to the headspace than observed for experiments B at the same flow rate (67% vs 74% for experiments B and C at 0.88 mL/min). However, as the flow rates increase from C1 (0.88 mL/min) to C4 (8.8 mL/min), the proportion of CO_2 which reaches the headspace increases from 67% to 93%. The presence of sand and the injection rate both effect the fate of the released gases and therefore the gas concentration in the headspace, with less gas dissolution or trapping at higher injection rates.

For experiments B and C we calculate that between 1% and -6% of CH_4 is retained in the sediment or water (i.e. dissolved or trapped, and so does not reach atmosphere). These negative factors are very small, and are likely within experimental error.

	R_{hyp} (ppm/hr)		**R_{obs} (ppm/hr)**		**Proportion that reached the headspace**		**Proportion that did not reach the headspace**	
	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4
A			173	47	n/a	n/a	n/a	n/a
B	246	67	181	71	74%	106%	26%	-6%
C1	260	71	174	72	67%	101%	33%	-1%
C2	599	142	451	145	75%	102%	25%	-2%
C3	1299	355	1214	362	93%	102%	7%	-2%
C4	2598	710	2418	703	93%	99%	7%	1%

Table 2*: We calculate gas fate by comparing the initial rate of increase in gas concentrations in the headspace observed (R_{obs}) with the rate predicted (R_{hyp}) if none of the gas dissolves into the water or is residually trapped in the sand (for the given gas mixture and flow rate).*

While control experiment A shows negligible temporal difference in the rate of change in gas concentration, for experiments B and C there is modest 5-10% decline in the rate (Figure 4). This decline may be attributed to changes in the water chemistry (e.g. pH and dissolved gas concentration), either as gas dissolves into water while ascending through the sediment and water column, or as gas in the headspace dissolves into the water during the course of the experiments. For experiments C2-C4, the rate of decline in concentration is similar to B and C1 on a percentage basis. The water column depth is also less in experiment C than in B, but this does not appear to affect the quantity of CO_2 that reaches the headspace.

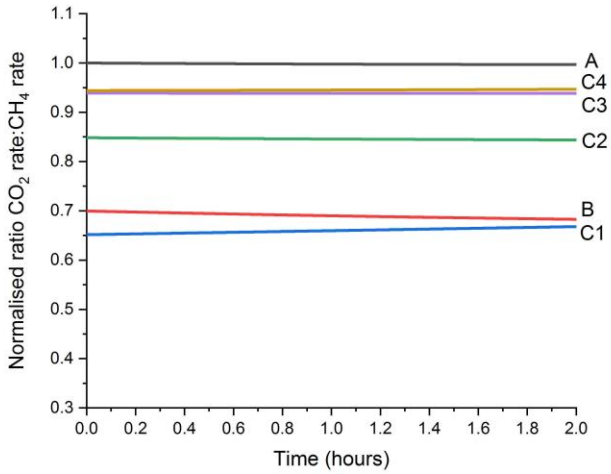

***Figure 4**: The normalised ratio of the CO_2 rate:CH_4 rate for all experiments. The ratios have been normalised relative to the initial ratio (i.e. 3.68) obtained for the control experiment (A).*

The presence of water and both water and sand in experiments B and C each have a significant impact on the ratio of the rates of CO_2 and CH_4, see Figure 4. For B, at 0.88 mL/min injection rates the normalised gas ratio reaches a constant value of ~0.70 with a very modest decrease during the duration of the experiment. For the experiments with sand and water, the ratios increase from 0.65 to 0.88 as the flow rate is increased from 0.88 mL/min to 8.80 mL/min. That is, the proportion of CO_2 that either dissolves or is residually trapped decreases. Interestingly, there is little difference in the ratio between experiments B and C for 0.88 mL/min flow rate. The only observable difference in degassing style between experiments B and C is the irregularity of the bubbling, which makes concentration increase more intermittent in C.

4. Discussion

Our results shed light on the conditions and processes that affect the fate of CO_2 and has implications for how tracers may be used to detect and quantify CO_2 leak rates in aqueous environments.

4.1 Fate of injected gases

The control experiment A where a constant rate of increase in concentration is observed confirms that leakage from the pond through the lid is minimal even towards the end of the experiments. The start of the experiment, when the headspace concentrations are low (and when leakage is minimal), is the most relevant to real-world conditions when leakage establishes into an open environmental system.

Our experiments show that the CH_4 is a conservative tracer under these laboratory conditions. The negligible difference between the quantity of CH_4 injected and the quantity that reaches the headspace indicates that the amount of CH_4 that is interacting with the water column and dissolving in the water is so small that it is undetectable within experimental error. This is expected; the solubility of CH_4 in water is ~two orders of magnitude less than CO_2 at room temperature and pressure (Yalkowsky et al., 2010). As such, determining the fate of the injected CH_4 is relatively straight forward: trace quantities may become residually trapped in the sediments and/or may dissolve, but the majority migrates in bubble form through the water column to be released into the headspace. There is a possibility that very small quantities of methane are being generated or digested by

methane-utilizing or methane-generating bacteria. We reduced the likelihood of this by using deionised water and clean sand, and by conducting experiments in a controlled and access-restricted laboratory.

In contrast to CH_4, there are a several fates for the injected CO_2 since it is comparatively more soluble. Proportions of CO_2 may become trapped in the sediments, dissolve into pore waters, dissolve into the water column during bubble ascent, or once the CO_2 is released into the headspace it may dissolve into the top layer of water. The decrease in rate of gas ratios in experiment B (see Figure 4) suggests that the latter may be occurring. There will be no carbonate precipitation given that clean silica sand is used for the experiments.

We observe in experiments C that the proportion of injected gas that reaches the headspace increases when gas flows through water saturated sand, and increases with gas injection rate. These findings can be understood by gas-fluid partitioning processes, which are a function of $Volume_{(gas)}/Volume_{(water)}$ (V_g/V_w) (see Darrah et al. (2014) and references therein). The total volume of water in experiments B (only water) is greater than C (sand and water). Thus, V_g/V_w is lower in experiment B, and there is greater dissolution potential for the gases. In C, the V_g/V_w conditions of the water saturated sand and the water column are different. In the water-saturated sand, the water volume relative to the gas volume is decreased, thereby inhibiting the dissolution capacity. Further, bubble nucleation increases as a function of surface area. Therefore, in the sand, the grain surfaces will enhance bubble nucleation and thus inhibits gas dissolution further.

The gas injection rate has a much stronger control on the gas fate than the presence of sand. At low release rates, less CO_2 reaches the headspace. Doubling the injection rate (from 0.88 to 1.76 mL/min, experiments C1 and C2 respectively) more than halves the quantity of CO_2 that does not reach the headspace (i.e. dissolves or is residually trapped), from 35% to 15%. And for 4.4 and 8.8 mL/min (experiments C3 and C4) the interaction between the CO_2 and water is minimal and is close to the control conditions (at only 5% loss).

When the injection rate is low, V_g/V_w is less, and so there is more potential for gas dissolution. Further, the gas pressure must build up sufficiently for the fluids to overcome the capillary pressure of the pore throat and allow gas flow, or to move the sand grains enabling bubble release. No one single leak pathway is established, otherwise the bubble intermittency would be cyclical, and this was not observed in our experiments with sand, where the bubbling style was irregular and intermittent.

Increasing the gas injection rate essentially increases V_g/V_w, which in turn reduces the gas dissolution capacity. The rate of bubble nucleation is more rapid, and flow is less intermittent as the gases soon overcome water pressures required for flow. As a result, the degree of interaction of the bubble and unsaturated water in the water column is be relatively limited, particularly if there is little to moderate mixing of the water column (and so mixing mostly occurs by diffusion).

This has important implications for detecting and quantifying seabed leakage above CO_2 stores. For low leak rates the relative concentration of CH_4 (or other inert tracer) in the bubbles will be much greater than the injected gas mixture, which could make it hard to estimate the initial leak rate. In contrast, if, at high leak rates, CO_2 attenuation due to dissolution is minimal during ascent through overburden sediments, then the surface quantitation of leakage will largely reflect the rate of leakage from the storage reservoir. That is, the quantity of CO_2 leaked could be approximated by simply measuring the rate of CO_2 leakage from gas bubbling.

As such, further work should strive to use traces to better understand the factors and variables that affect CO_2 fate for different leakage rates in different environments, by

varying injection rates and parameter such as different water depths, water chemistry and sediment properties (permeability, injection depth).

4.2 Style of gas release

We find that low release rate affects the style of emission in the presence of sand. At low gas flow, gas bubbling was irregular and intermittent. Periods of no bubbling were observed for up to ten minutes when gas was released at 0.88 mL/min in experiments C1. These periods of bubbling hiatus become shorter at higher release rates, but regular bubbling (like that observed in experiment B) isn't established even at 8.8 mL/min (C3).

This intermittency made our calculations of the evolution of gas seepage in experiments C complicated. Significant peaks were detected when bubbles broke the surface of the water, releasing the gas into the headspace. Even at faster gas release rates a polynomial needed to be fitted to the data to allow us to systematically study the results.

The irregular bubbling style that we simulated in experiments C is similar to observations at natural seeps that occur underwater, and particularly low flux systems. For example, CO_2 bubbling occurs at Laacher See, an onshore caldera lake in Germany. Bubble streams of CO_2 emerge from the base of the lake and also in shallow waters close to the Eastern shore. In these shallow waters, the diffuse flux is low (~54 g m^{-2} d^{-1} (Jones et al., 2009) in (Kirk, 2011)) and the bubble streams have been observed to change their position almost continuously (Caramanna, 2017, *pers comm*). Similarly, the locations of CO_2 bubble streams at low flux seeps in Daylesford (Victoria, Australia) are observed to turn on and off, and so bubbling is intermittent (Roberts et al., submitted). The methodologies developed for CCS that detect and quantify gas emission at aqueous seeps must be capable of doing both, even when gas release is intermittent and occurs at a point location (see (Roberts et al., 2018).

Seepage occurred at a very specific location in our experiments – directly above the release point. This has not been the case for a number of field CO_2 release experiments. For example, at QICS, a number of seep points established ~15 m NW of the injector (Blackford et al., 2014). Such deviation is attributed to the presence of heterogeneities in the sediments through which the CO_2 is migrating. That the seep point in our experiments was directly above the injector suggests that there were no structures in the sand that influenced the gas flow, however the injection depth in our lab experiments is a fraction of the injection depth at field experiments, and the sediments in our experiments were selected to be ~homogeneous.

4.3 Implications for CO_2 distribution and loss at QICS experiment

The conditions in experiment C were designed to mimic the QICS environment, with water depth and flow rate ~ 100^{th} of the scale, and sediments similar to the 2m thick fine sand at QICS. Maximum injection rate at QICS was 210 kg/d (~2.4 g/s, or 80,000 mL/min assuming standard conditions). 100^{th} of the injection rate at QICS is therefore ~800 mL/min. The injector pipe at QICS was 2 cm diameter, and so the injector pipe in the experiments is ~157 times smaller, but is not perforated like the pipe at QICS, making it difficult to compare the CO_2 flow rates per unit area from the pipe head. If we assume that the QICS pipe was not perforated, and so all gas was emitted from the injector, then 100^{th} of the injection rate per unit area is ~5 mL/min. The maximum injection rates in experiment C (8.8 ml/min of gas mixture; ~7.0 mL/min CO_2) therefore most closely mimicked the flow rate per unit area rather than the total release rate at the QICS site.

Determining the fate of CO_2 released during the QICS experiment was challenging; one field survey at maximum CO_2 injection rates estimated that ~15% of the injected CO_2 reached the seabed as a free phase, and geochemical modelling predicted that 14 - 63% dissolved in

sediment pore waters (Blackford et al., 2014; Taylor et al., 2015). Even at the smallest injection rate (0.7 mL/min CO_2), 1000th the maximum rate at QICS, only a third of the injected gas dissolved. Our experimental outcomes therefore imply that the technique to measure gaseous CO_2 emission at QICS (funnels sequentially placed over the bubbling points) vastly underestimated the quantity of CO_2 released as a gas.

However, there are significant differences in the experimental conditions that limit the extent to which our experiment outcomes can be used to infer CO_2 fate at QICS. For example, at QICS, the bubbles dissolved in the water column and did not break the seabed surface. In contrast, for experiment C the vast majority (>90%) of CO_2 was emitted as bubbles that reached the surface. Therefore much less CO_2 was dissolving in the lab experiments. Although the pond experiments used deionised water, not seawater (and salinity reduces CO_2 dissolution) there are many reasons why CO_2 dissolution could be much greater at QICS compared to a scaled-down lab experiment. First, the pressures and temperature conditions differ significantly between the field and lab experiments; water and sediment depth was much deeper at the field site, so the pressure environment was much greater, which would enhance CO_2 dissolution compared to the pond experiments in the lab. Second, summer seawater temperatures in Ardmucknish Bay were much cooler than in the lab (ranging from 10-14℃ during the release experiment (Atamanchuk et al., 2015) whereas the labs are maintained at 22.5℃) and cooler water temperature also enhances CO_2 dissolution. Further, the overburden at the QICS site was heterogeneous, with sediment layers that varied in permeability properties, the most permeable of which was the upper unit, B, which we selected sand in the experiment to imitate. Although gas bubbles were observed within 24 hours of starting injection at QICS, an accumulation of gas was imaged in the subsurface. In contrast, CO_2 in the lab experiments was injected into structureless, high porosity unconsolidated sands, which would offer very little barrier to CO_2 flow and emission. As such, results from the lab experiments cannot be used to infer the likely fate of CO_2 at QICS. However, the results can shed light on whether and how gas tracers could be used to determine the fate of CO_2 that leaks into the marine environment.

4.4 Using CH_4 as a tracer for leak quantitation

The presence of water, or water saturated sand, in a gas leak system significantly influences the gas fate, and presents challenges for developing reliable methods to identify and quantify any leaks that might arise from geological CO_2 stores. Our experiments show that CH_4, a common constituent of CO_2 streams and subsurface reservoirs, could be used as a chemical tracer to determine the fate or loss of CO_2, if the leaking gases are sampled either at the sea or lake bed, or at the water surface (if the bubbles reach surface). For our experimental conditions, CH_4 has negligible interaction with the water column, and so by knowing the inherent ratio between CO_2 and CH_4 a calculation of the total amount of CO_2 leaking can be quantified.

However, demonstrating the capability of CH_4 as a tracer for CO_2 fate and quantitation does not render it appropriate for reliable use as a tracer for CCS in natural systems. In the case of these experiments, CH_4 was selected because it can also be sourced, used and detected relatively easily and at low cost – particularly since CH_4 is present at trace levels in the atmosphere. However, the experiments are simplistic; water and sand volumes are small, we use deionised water rather than saline water, and the water temperature is much warmer than most sea water temperatures globally. A wealth of studies have been published which examine the relative utility of chemical tracers such as CH_4 in natural systems, for CCS and other applications (Myers et al., 2013; Roberts et al., 2017; Stalker and Myers, 2014). Tracer chemicals for CO_2 leakage would ideally be conservative, have no effect on CO_2 fluid flow, and cause no negative environmental impacts should they leak to surface.

CH_4 can affect the gas plume and migration, with implications for storage integrity (Soltanian et al., 2018). In our experiments, CH_4, being more buoyant and insoluble, may facilitate the formation of smaller bubbles than if the gas had a greater proportion of CO_2 (McGinnis et al., 2011). The methane may therefore be affecting not only the size of the bubbles, but how rapidly they rise through the sand/water column. Bubble size and bubble velocity affects dissolution; therefore a CH_4-CO_2 system will be different from 100% CO_2.

Tracers would also ideally not be naturally present, or generated in, the subsurface. However, CH_4 is present in many natural subsurface systems, at depth and near the surface. Further, methane is itself a strong greenhouse gas, over 36 times more potent than CO_2 (Myhre et al., 2013) and can have other negative environmental effects (Roberts et al., 2017). There is also potential for CH_4 to be consumed by methanophiles in the aqueous environment prior to being detected (Roberts et al., 2017). CH_4 is not a completely conservative tracer. Calculations of leakage using CH_4 as a tracer would require that the relative solubility of the two gases in the lake or sea bed conditions are known. The solubility of CH_4 in freshwater is ~130 times less than CO_2 (Yalkowsky et al., 2010), however CO_2 is much less soluble in brines or seawater, and the relative solubility of the two gases is reduced. Temperature and pressure will affect the solubility of the two gases differently, and these effects must be characterised for the sea or lake bed, as well as the vertical profile from injection formation to the surface.

Further, to be a low-cost and easily deployed tracer, CH_4 must be present in the captured CO_2 stream, thereby avoiding the cost and potential environmental risks associated with adding a tracer. CH_4 is a common constituent of pre-combustion CO_2 capture from coal or biomass; CO_2 streams from these sources typically contain ~100 ppmv CO_2 Porter et al., 2016 (Porter et al., 2016). However, depending on the specifics of the capture process itself, the CH_4 may be present in <1 ppmv concentrations (Porter et al., 2015). CO_2 streams from oxyfuel combustion, post-combustion capture and Direct Air Capture are not reported to contain CH_4 traces, and the only other industrial process with trace CH_4 in the CO_2 stream is coke production (Porter et al., 2015). As such, CH_4 is not a reliable constituent of CO_2 from all capture processes, and its concentrations, if present, will be site specific and may vary with time, particularly if the raw fuel is changing. That said, it is not clear whether or not the flue gases reported in Porter et al. 2015 are tested for trace (bbp) concentrations of CH_4, and trace quantities might be sufficient for using CH_4 as a tracer.

For these reasons, it would likely be problematic to use to unequivocally identify and quantifying CO_2 leakage. While it is probable that other inert tracers (i.e. not CH_4) might be selected for use at commercial CCS stores, our work quantitatively demonstrates how tracers more generally could be used to determine CO_2 fate and quantitation offshore. Further, potential chemical tracers for CCS should be as inert as practical and indigenous to the CO_2 stream to minimise cost, and for these reasons CH_4 might be considered appropriate. However future work should explore the application and sampling of other preferred tracers including inherent CO_2 isotopes and noble gases (Flude et al., 2016; Roberts et al., 2017). Noble gases have been used to determine CO_2 origin and fate in natural analogues for CO_2 reservoirs and leak sites (Gilfillan et al., 2008; Wilkinson et al., 2009) but, to date, have not yet been used to quantify leakage from natural or artificial systems.

5. Conclusion

We have explored how well chemical tracers for CCS can aid the quantitation of CO_2 leakage and CO_2 fate in aquatic environments. To date, monitoring approaches to quantify CO_2 leaks to surface have largely been explored for terrestrial environments. Our experiments

simulated gas leakage into sediments that mimic the seabed and we measured the fate and partitioning of co-released gases into water, and into sand and water, at different flow rates. As the inherent ratio of CH_4 and CO_2 is known, the leak rate and fate of CO_2 can be accurately determined from the gas ratio within the gas bubbles that leak to surface. We use methane as it is low cost and easy to measure in situ, and it is a candidate tracer for CCS, but we recognise that more inert compounds may be more desirable for use as commercial tracers.

We have found that the fate of the CO_2 (i.e. the degree of CO_2 dissolution) is affected by the leakage rate more than the physical conditions of the aqueous leakage pathway (i.e. the presence of sand). Doubling the injection rate reduces the proportion of CO_2 dissolved by over half (from 35% to 15%), whereas the introduction of sand only increases the quantity of CO_2 that dissolves from 28% to 35%. While further work needs to be done to accurately quantify the effects on the fate of CO_2 and tracers for varying depths of water, water chemistry and sediment thickness, our results suggest that conservative tracers could be used to successfully deduce the fate and quantity of CO_2 leaks should leakage to surface occur in marine or aquatic environments.

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Data Availability Statement

All experimental data is publicly available via the UKCCSRC Data and Information Archive: DOI [insert DOI]

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Highlights

A large proportion of global CO_2 storage capacity is located offshore

Quantifying CO_2 leaks into aquatic environments is challenging

Our experiments test methane as a chemical tracer for CO_2 leakage to sea or lake bed

We find that bubble stream gas content can inform CO_2 leak rate and fate

The proportion of CO_2 dissolution is affected by leak style